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# Electrochromic properties of niobium oxide thin films prepared by radio-frequency magnetron sputtering method

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Electrochromic niobium oxide thin films were prepared by a radio-frequency magnetron sputtering method. Amorphous  $\text{Nb}_2\text{O}_5$  thin films deposited at radio-frequency power 100 W showed the electrochromic behavior: Reduction and oxidation of the films in 0.1 M  $\text{Na}_2\text{CO}_3 + 0.1 \text{ M NaHCO}_3$  buffer solution resulted in coloration and bleaching, respectively. Coulometry indicated that the coloration efficiency was  $10 \text{ cm}^2/\text{C}$ .

One of the group *V-B* oxide, niobium oxide ( $\text{Nb}_2\text{O}_5$ ), exhibits electrochromism like that of tungsten oxide  $\text{WO}_3$ . The electrochromic niobium oxide films were electrochemically formed by an anodic oxide growth on a niobium electrode.<sup>1</sup> However, little work has been performed on this system to qualify it for thin film use in optical shutters.

This letter shows the electrochemical and optical properties of the  $\text{Nb}_2\text{O}_5$  thin films prepared by the radio-frequency (rf) magnetron sputtering method.<sup>2</sup> The optical properties are studied under electrochemical polarization *in situ* in spectroelectrochemical cells.

The  $\text{Nb}_2\text{O}_5$  film was deposited on a transparent electrode. The electrode substrates were  $0.9 \times 5 \text{ cm}^2$  pieces of glass with a conductive coating of a fluorine-doped tin oxide ( $\text{SnO}_2\text{:F}$ , FTO) on one side (Nippon Sheet Glass Co. Ltd.).

In preparing  $\text{Nb}_2\text{O}_5$  films, rf magnetron sputtering equipment (Osaka Vacuum Co. Ltd.) was used with a  $\text{Nb}_2\text{O}_5$  powder (Taki Chemical Co., Ltd.) target. The sputtering gas was an argon-oxygen mixture ( $\text{Ar}/\text{O}_2 = 4/1$ ). The flow rate of the sputtering gas was 30 sccm. Before sputtering, the chamber was evacuated to  $2 \times 10^{-6}$  Torr. The target was presputtered for 10 min. During sputtering, the substrate was water cooled, and the chamber pressure was kept at  $3.0 \times 10^{-3}$  Torr. The deposited film thickness was adjusted to about 50–200 nm by selecting an appropriate sputtering time.

The crystallinity of the film was analyzed by x-ray diffraction with  $\text{Cu K}\alpha$  radiation. The electrochromic behavior was evaluated using a sample cell that was installed in the sample compartment of a spectrophotometer. The sample cell was made of a standard quartz cuvette with a

1-cm pathlength. An electrode active area of  $0.5 \text{ cm}^2$  was used in these experiments. The counterelectrode was  $\text{SnO}_2\text{:F}$  film coated on the glass plates. The electrolyte used was a 0.1 M  $\text{Na}_2\text{CO}_3 + 0.1 \text{ M NaHCO}_3$  buffer solution.<sup>1</sup> The reference compartment contained a cuvette filled with electrolyte and a pair of electrodes of  $\text{SnO}_2\text{:F}$  film coated onto the glass plates. Thus, the transmittance measurements of the  $\text{Nb}_2\text{O}_5$  electrode included contributions from only the  $\text{Nb}_2\text{O}_5$  film. A voltage of  $\pm 3.0 \text{ V}$  was applied between the electrodes. Cyclic voltammetry was done by using a potentiostat and a function generator at a potential sweep rate of  $70 \text{ mV/s}$  from  $-1900 \text{ mV}$  to  $+500 \text{ mV}$  vs SCE (standard calomel electrode). A saturated calomel reference electrode with extended Luggin capillary was used. The amount of moving charge was measured with a Coulometer.

The  $\text{Nb}_2\text{O}_5$  films deposited under the deposition condition of this study (rf power  $< 300 \text{ W}$ ) were confirmed by x-ray diffraction usually in the amorphous state. Figure 1 shows the x-ray diffraction pattern of the 200 nm thick  $\text{Nb}_2\text{O}_5$  film on a FTO-coated glass substrate for rf power 300 W. No trace of peaks for  $\text{Nb}_2\text{O}_5$  is observed.

The  $\text{Nb}_2\text{O}_5$  films were transparent. The optical energy gap of the  $\text{Nb}_2\text{O}_5$  film was estimated from the optical absorption measurements for 50 nm thick amorphous films, which were deposited at two different rf powers. Figure 2 shows the absorption coefficients as a function of photon energy. The extrapolations to abscissa show an optical energy gap  $E_g$  of about 3.8 eV.

Figure 3 shows the cyclic voltammogram of the 157

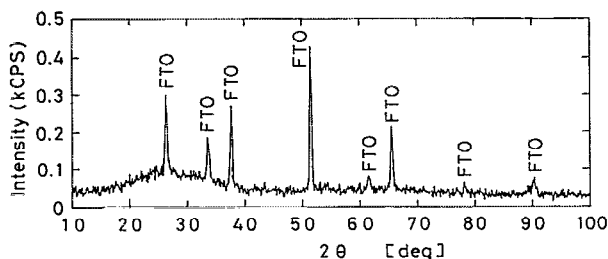


FIG. 1. X-ray diffraction pattern of the 200 nm thick  $\text{Nb}_2\text{O}_5$  film deposited at rf power 300 W on a FTO-coated borosilicate glass substrate.

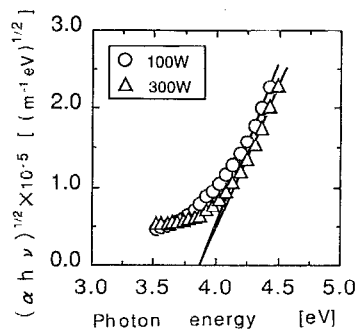


FIG. 2. Relation between absorption coefficient and energy of incident photon.

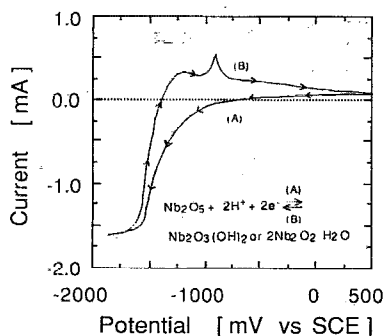


FIG. 3. Cyclic voltammogram of the  $\text{Nb}_2\text{O}_5$  film in 0.1 M  $\text{Na}_2\text{CO}_3$  + 0.1 M  $\text{NaHCO}_3$  buffer solution at a sweep rate of 70 mV/s.

nm thick  $\text{Nb}_2\text{O}_5$  film. The anodic peak appears at approximately  $-900$  mV (SCE), while the cathodic peak appears at about  $-1500$  mV (SCE), respectively. Coloration (upon reduction) and bleaching (upon oxidation) are associated with redox peaks at potentials in the range observed for the  $\text{Nb}_2\text{O}_5$  redox couple. In an electrolyte, the following reaction<sup>1</sup> is postulated to describe the film conversion process:

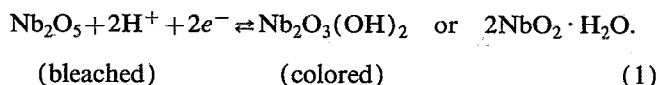


Figure 4 shows the optical transmittance spectra of the as-deposited, reduced (colored), and oxidized (bleached) niobium oxide films sputtered at rf power 100 W on FTO-coated glass substrates. In the as-deposited state, the film is

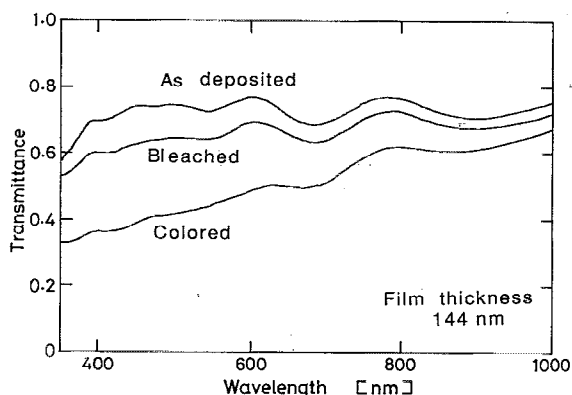


FIG. 4. Optical transmittance spectra of a  $\text{Nb}_2\text{O}_5$  film in the as-deposited, reduced (colored), and oxidized (bleached) states.

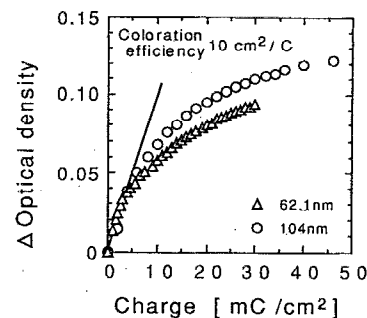


FIG. 5. Change in optical density at a wavelength of 550 nm as a function of charge density.

essentially transparent, but upon reduction (on application of  $-3.0$  V) it produced a marked change in light absorption throughout the visible wavelength region of the spectrum. The change can be removed on oxidation (on application of  $+3.0$  V). The transmittance of the bleached film is lower than that of the as-deposited film.

Thus, the  $\text{Nb}_2\text{O}_5$  film sputtered at 100 W exhibited clear electrochromism. However, the films sputtered at 200 and 300 W showed no change in transmittance by applying voltage. This is postulated to be caused by the substrate temperature rise due to the high rf power during sputtering. In order to observe electrochromism in  $\text{WO}_3$ , it has been reported that the substrate temperature must be kept lower than  $100^\circ\text{C}$  when preparing films by the sputtering method.<sup>3</sup>

The change in optical density for  $\lambda = 550$  nm as a function of injected charge density is shown in Fig. 5. The slope of the linear part, i.e., change in optical density divided by the injected charge density, gives the value of the coloration efficiency. The coloration efficiency of the sputtered  $\text{Nb}_2\text{O}_5$  film is  $10 \text{ cm}^2/\text{C}$ .

In conclusion, electrochromic niobium oxide thin films were prepared in air by a rf magnetron sputtering method. Amorphous thin films deposited at rf power 100 W showed the electrochromic behavior: Reduction and oxidation of the films in 0.1 M  $\text{Na}_2\text{CO}_3$  + 0.1 M  $\text{NaHCO}_3$  buffer solution resulted in coloration and bleaching, respectively. Coulometry indicated that the coloration efficiency was  $10 \text{ cm}^2/\text{C}$ .

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